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APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A
FILING DATE UNDER 35 USC 111.**

APPLICATION NUMBER: 60/542,089

FILING DATE: February 05, 2004

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PRIORITY DOCUMENT

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Certifying Officer



17698 U.S. PTO

Practitioner's Docket No. U 015022-9

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: **ANDRÉ PETER STEYNBERG**

For: **HYDROCARBON SYNTHESIS**

Mail Stop Provisional Patent Application
Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

Optional Customer No. Bar Code



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PATENT TRADEMARK OFFICE

17354 U.S. PTO
60/542089



COVER SHEET FOR FILING PROVISIONAL APPLICATION
(37 C.F.R. § 1.51(c)(1))

WARNING: *"A provisional application must also include the cover sheet required by § 1.51(c)(1) or a cover letter identifying the application as a provisional application. Otherwise, the application will be treated as an application filed under paragraph (b) [nonprovisional application] of this section." 37 C.F.R. § 1.53(c)(1).. See also M.P.E.P. § 201.04(b), 6th ed., rev. 3.*

CERTIFICATION UNDER 37 C.F.R. 1.10*

(Express Mail label number is mandatory.)

(Express Mail certification is optional.)

I hereby certify that this correspondence and the documents referred to as attached therein are being deposited with the United States Postal Service on February 5, 2004, in an envelope as "EXPRESS MAIL POST OFFICE TO ADDRESSEE" service under 37 C.F.R. 1.10 Mailing Label Number EV 327552178 US addressed to the Commissioner for Patents, P. O. Box 1450, Alexandria, VA 22313-1450.

CYNTHIA PADGETT

(type or print name of person mailing paper)

Cynthia Padgett

Signature of person mailing paper

WARNING: *Certificate of mailing (first class) or facsimile transmission procedures of 37 C.F.R. 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence.*

***WARNING:** *Each paper or fee filed by "Express Mail" must have the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 C.F.R. 1.10(b).*

"Since the filing of correspondence under § 1.10 without the Express Mail mailing label thereon is an oversight that can be avoided by the exercise of reasonable care, requests for waiver of this requirement will not be granted on petition." Notice of Oct. 24, 1996, 60 Fed. Reg. 56,439, at 56,442.

NOTE: "A complete provisional application does not require claims since no examination on the merits will be given to a provisional application. However, provisional applications may be filed with one or more claims as part of the application. Nevertheless, no additional claim fee or multiple dependent claims fee will be required in a provisional application." Notice of December 5, 1994, 59 FR 63951, at 63953.

"Any claim filed with a provisional application will, of course, be considered part of the original provisional application disclosure." Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,209.

NOTE: "A provisional application is not entitled to the right of priority under 35 U.S.C. 119 or 365(a) or § 1.55, or to the benefit of an earlier filing date under 35 U.S.C. 120, 121 or 365(c) or § 1.78 of any other application. No claim for priority under § 1.78(a)(3) may be made in a design application based on a provisional application. No request under § 1.293 for a statutory invention registration may be filed in a provisional application. The requirements of §§ 1.821 through 1.825 regarding application disclosures containing nucleotide and/or amino acid sequences are not mandatory for provisional applications." 37 C.F.R. 1.53(c)(3).

NOTE: "No information disclosure statement may be filed in a provisional application." 37 C.F.R. § 1.51(d). "Any information disclosure statements filed in a provisional application would either be returned or disposed of at the convenience of the Office." Notice of December 5, 1994, 59 FR 63591, at 63594.

NOTE: "No amendment other than to make the provisional application comply with the patent statute and all applicable regulations, may be made to the provisional application after the filing date of the provisional application." 37 C.F.R. § 1.53(c).

NOTE: 35 U.S.C. 119(e) provides that "[i]f the day that is 12 months after the filing date of a provisional application falls on a Saturday, Sunday, or Federal Holiday within the District of Columbia, the period of pendency of the provisional application shall be extended to the next succeeding secular or business day."

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 C.F.R. § 1.51(c)(1)(i).

1. The following comprises the information required by 37 C.F.R. § 1.51(c)(1):
2. The name(s) of the inventor(s) is/are (37 C.F.R. § 1.51(c)(1)(ii)):

NOTE: "If the correct inventor or inventors are not named on filing, a provisional application without a cover sheet under § 1.51(c)(1), the later submission of a cover sheet under § 1.51(c)(1) during the pendency of the application will act to correct the earlier identification of inventorship." 37 C.F.R. § 1.48(f)(2).

NOTE: "The naming of inventors for obtaining a filing date for a provisional application is the same as for other applications. A provisional application filed with the inventors identified as 'Jones et al.' will not be accorded a filing date earlier than the date upon which the name of each inventor is supplied unless a petition with the fee set forth in § 1.17(i) is filed which sets forth the reasons the delay in supplying the names should be excused. Administrative oversight is an acceptable reason. It should be noted that for a 35 U.S.C. 111(a) application to be entitled to claim the benefit of the filing date of a provisional application the 35 U.S.C. 111(a)[.] application must have at least one inventor in common with the provisional application." Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,209.

The term "invention" is typically used to refer to subject matter which applicant is claiming in his/her application. Because claims are not required in a provisional application, it would not be appropriate to reference joint inventors as those who have made a contribution to the "invention" disclosed in the provisional application. If the "invention" has not been determined in the provisional application because no claims have been presented, then the name(s) of those person(s) who have made a contribution to the subject matter disclosed in the provisional application should be submitted. Section 1.45(c) states that "if multiple inventors are named in a provisional application, each named inventor must have made a contribution, individually or jointly, to the subject matter disclosed in the provisional application." All that § 1.45(c) requires is that if someone is named as an inventor, that person must have made a contribution to the subject matter disclosed in the provisional application. When applicant has determined what the invention is by the filing of the 35 U.S.C. 111(a) application, that is the time when the correct inventors must be named. The 35 U.S.C. 111(a) application must have an inventor in common with the provisional application in order for the 35 U.S.C. 111(a) application to be entitled to claim the benefit of the provisional application under 35 U.S.C. 119(e). Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,208.

See 37 C.F.R. § 1.53.

1.	<u>ANDRÉ</u>	<u>PETER</u>	<u>STEYNBERG</u>
	GIVEN NAME	MIDDLE INITIAL OR NAME	FAMILY (OR LAST) NAME
2.	<u></u>	<u></u>	<u></u>
	GIVEN NAME	MIDDLE INITIAL OR NAME	FAMILY (OR LAST) NAME
3.	<u></u>	<u></u>	<u></u>
	GIVEN NAME	MIDDLE INITIAL OR NAME	FAMILY (OR LAST) NAME

3. Residence address(es) of the inventor(s), as numbered above (37 C.F.R. § 1.51(c)(1)(iii)):

1. 3 ORANGE RIVER STREET, SE4, VANDERBIJLPARK, 1911, REPUBLIC OF SOUTH AFRICA
 2.
 3.

4. The title of the invention is (37 C.F.R. § 1.51(c)(1)(iv)):

HYDROCARBON SYNTHESIS

5. The name, registration, customer and telephone numbers of the practitioner (if applicable) are (37 C.F.R. § 1.51(c)(1)(v)):

Name of practitioner: CLIFFORD J. MASS

Reg. No. 30,086

Customer No. 00140

Tel. (212) 708-1890

(complete the following, if applicable)

☐ A power of attorney accompanies this cover sheet.

6. The docket number used to identify this application is (37 C.F.R. § 1.51(c)(1)(vi)):

Docket No. U 015022-9

7. The correspondence address for this application is (37 C.F.R. § 1.51(c)(1)(vii)):

Ladas & Parry, 26 West 61st Street, New York, NY 10023

8. Statement as to whether invention was made by an agency of the U.S. Government or under contract with an agency of the U.S. Government. (37 C.F.R. § 1.51(c)(1)(viii)).

This invention was made by an agency of the United States Government, or under contract with an agency of the United States Government.

☒ No
☐ Yes

The name of the U.S. Government agency and the Government contract number are:

9. Identification of documents accompanying this cover sheet:

A. Documents required by 37 C.F.R. §§ 1.51(c)(2)-(3):

Specification:

No. of pages 14

Drawings:

No. of sheets 1

B. Additional documents:

☐

Claims:

No. of claims

Note: See 37 C.F.R. § 1.51.

☐

Power of attorney

☐

Small Entity Statement or Written Assertion

☐

Assignment

☐

English language translation of non-English provisional application and
Statement of Accuracy thereof

NOTE: A provisional application which is filed in a language other than English, does not have to have an English language translation. See 37 C.F.R. § 1.52(d)(2). However, if the provisional application is not in the English language and will later serve as a benefit of its filing date for a nonprovisional application, other than a design patent, or for an international application designating the U.S., then an English language translation must be filed in the provisional application or the later filed nonprovisional application. See § 1.78(a)(5)(iv).

10. Fee

The filing fee for this provisional application, as set in 37 C.F.R. § 1.16(k), is \$160.00, for other than a small entity, and \$80.00, for a small entity.

☒ Applicant is not a small entity.

☐ Applicant is a small entity.

NOTE: "A . . . statement of compliance with existing § 1.27 is required to be filed in each provisional application in which it is desired to pay reduced fees." Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,197.

11. Small entity assertion

☐ A Statement or Written Assertion that this is a filing by a small entity under 37 C.F.R. § 1.27(c)(1) is attached.

☐ Small entity status is asserted for this application by payment of the small entity filing fee under § 1.16(k). 37 C.F.R. § 1.27(c)(3).

***WARNING:** "Small entity status must not be established unless the person or persons signing the . . . statement can unequivocally make the required self-certification." M.P.E.P. Section 509.03, 6th ed., rev. 2, July 1996 (emphasis added).*

12. Fee payment

☒ Fee payment in the amount of \$ 160.00 is being made at this time.

☐ No filing fee is to be paid at this time. (This and the surcharge required by 37 C.F.R. § 1.16(l) can be paid subsequently.)

13. Method of fee payment

- ☒ Check in the amount of \$ 160.00.
☐ Charge Account No. 12-0425, in the amount of \$ _____.
A duplicate of this Cover Sheet is attached.

Please charge Account No. 12-0425 for any deficiency in the fee paid.

Date: _____

Tel.: ()

Date: February 5, 2004

Reg. No.: 30,086

Tel.: (212)708-1890

Customer No.: 00140

Signature of submitter

OR

Signature of practitioner

CLIFFORD J. MASS.
(type or print name of practitioner)

LADAS & PARRY
P.O. Address

26 WEST 61ST STREET
NEW YORK, NEW YORK 10023

UNITED STATES OF AMERICA

SPECIFICATION

TO ALL WHOM IT MAY CONCERN, BE IT KNOWN THAT:

STEYNBERG, André Peter

has invented a certain

"HYDROCARBON SYNTHESIS"

of which the following is a specification

THIS INVENTION relates to hydrocarbon synthesis. In particular, it relates to a process for synthesising hydrocarbons.

According to the invention, there is provided a process for synthesising hydrocarbons, which process includes

feeding a gaseous feedstock comprising hydrogen, carbon monoxide and carbon dioxide, into a dimethyl ether (DME) synthesis stage;

in the DME synthesis stage, converting a portion of the gaseous feedstock into a DME product and gaseous products;

separating the DME product from unreacted gaseous reactants and the gaseous products to obtain a tail gas comprising hydrogen and carbon monoxide;

feeding the tail gas into a Fischer-Tropsch hydrocarbon synthesis stage; and

allowing the hydrogen, carbon monoxide and carbon dioxide at least partially to react catalytically in the Fischer-Tropsch hydrocarbon synthesis stage to form hydrocarbons.

The Fischer-Tropsch hydrocarbon synthesis stage may be a two-phase high temperature catalytic Fischer-Tropsch hydrocarbon synthesis stage, the hydrocarbons formed in the Fischer-Tropsch hydrocarbon synthesis stage thus being gaseous hydrocarbons at the operating pressure and temperature of the Fischer-Tropsch hydrocarbon synthesis stage.

The process may include adjusting the composition of the gaseous feedstock so that the gaseous feedstock has a syngas number (SN) between 1.8 and 2.2, where

$$SN = \frac{[H_2] - [CO_2]}{[CO] + [CO_2]}$$

and where $[H_2]$, $[CO]$ and $[CO_2]$ respectively are the molar proportions of hydrogen, carbon monoxide and carbon dioxide in the gaseous feedstock.

Preferably, the syngas number is between 1.85 and 2.15, more preferably between 1.9 and 2.1, e.g. about 2.

Adjusting the composition of the gaseous feedstock may include removing some CO_2 from the gaseous feedstock. Thus, the syngas number may be adjusted upwardly. As will be appreciated, the gaseous feedstock can be derived from a methane-containing gas such as natural gas, or it can be derived from solid carbonaceous material such as coal. When the gaseous feedstock is derived from a carbonaceous material, such as coal, it is expected that, in a preferred embodiment of the process, CO_2 will be removed from the gaseous feedstock. In an optional embodiment of the invention, CO_2 is removed from the gaseous feedstock when the gaseous feedstock is derived from a methane-containing gas.

Removing some CO_2 from the gaseous feedstock may include absorbing CO_2 in a solvent, e.g. a Benfield solution. The process may thus also include recovering the removed CO_2 , by stripping the CO_2 from the solvent. This may be achieved, for example, by using a stripping gas and elevating the temperature of the solvent.

Instead, or in addition, adjusting the composition of the gaseous feedstock may include adding an H_2 rich gas to the gaseous feedstock.

Adding an H_2 rich gas to the gaseous feedstock may include reforming a portion of the gaseous feedstock in a steam reforming stage to produce an H_2 rich reformed gas, and combining at least some of the H_2 rich reformed gas with the gaseous feedstock being fed to the DME synthesis stage.

Typically, an installation for synthesising hydrocarbons which employs a Fischer-Tropsch hydrocarbon synthesis stage includes a hydroprocessing facility, which in turn relies on a steam reforming facility to generate H_2 for hydroprocessing. Advantageously, the process of the invention can thus rely on such a steam reforming

facility, possibly upgraded if necessary, also to provide H₂ rich reformed gas with which the composition of the gaseous feedstock can be adjusted, if necessary.

As mentioned hereinbefore, the gaseous feedstock may be derived from a methane-containing gas. Derivation of the gaseous feedstock may include reforming the methane-containing gas in a reforming stage in the presence of oxygen and steam. The reforming stage may be an autothermal reforming stage. Preferably, a low steam to carbon ratio of between about 0.2 and about 0.6, e.g. about 0.4, is used in the autothermal reforming stage. Instead, the reforming stage may be a catalytic or a non-catalytic partial oxidation stage, in which a steam to carbon ratio of 0.2 or less is typically used.

When derived from a methane-containing gas, the gaseous feedstock may comprise hydrogen and carbon monoxide in a molar ratio of between about 2.1 and about 2.3. When derived from a solid carbonaceous material, and relying on gasification of the solid carbonaceous material in a gasification stage, the gaseous feedstock typically has an H₂/CO molar ratio of between about 0.7 and about 2.1, often between about 0.7 and about 2.0.

Converting a portion of the gaseous feedstock into a DME product and gaseous products typically includes contacting the gaseous feedstock with a methanol catalyst and a methanol dehydration catalyst. The DME synthesis stage may thus include a methanol reactor followed by a methanol dehydration reactor. Instead, the methanol reactor may be dispensed with, or made smaller, with the DME synthesis stage including a combined methanol and methanol dehydration reactor. Thus, the DME product may be produced by use of a catalyst active in both the synthesis of methanol from the gaseous feedstock and methanol dehydration.

As methanol catalyst, a copper-containing catalyst is usually employed. Suitable catalysts however include compositions containing copper, zinc oxide, chromia, and/or alumina and possibly other oxidic materials such as magnesia.

Methanol dehydration catalysts usually comprise alumina or alumina silicates as active compounds.

The DME product typically includes a mixture of DME and methanol. If desired, the DME product can be subjected to a rectification process to recover a DME product with a desired purity. Typically, however, the process includes converting the DME product into light olefins, e.g. C_2 - C_4 olefins, in a light olefins production stage without increasing the DME concentration in the DME product.

The process may include recycling a portion of the tail gas from the DME synthesis stage to the DME synthesis stage. Typically, this recycle is less than the recycle encountered in a conventional stand-alone process for the production of DME. Thus, it is expected that a suitable ratio of tail gas recycle to gaseous feedstock will be between about 0 : 1 and about 2 : 1, preferably less than 1.1.

Overall $CO + CO_2$ conversion in the DME synthesis stage may be between about 20 % and about 80 %, preferably between about 40 % and about 60 %, e.g. about 50 %.

The DME synthesis stage may be operated at a pressure of 50 bar(g) or less, preferably at a pressure between about 20 bar(g) and about 50 bar(g), e.g. about 35 bar(g).

The tail gas from the DME synthesis stage typically includes unreacted hydrogen, unreacted carbon monoxide, carbon dioxide, and possibly other gaseous products. Advantageously, the carbon monoxide, carbon dioxide and hydrogen are then converted in the Fischer-Tropsch hydrocarbon synthesis stage to valuable hydrocarbons.

The gaseous hydrocarbons and any unreacted hydrogen, unreacted carbon monoxide, and CO_2 are withdrawn from the Fischer-Tropsch hydrocarbon synthesis stage, and may be separated into one or more condensed liquid hydrocarbon streams, a reaction water stream and a Fischer-Tropsch hydrocarbon synthesis stage tail gas.

The process typically includes recycling some of the Fischer-Tropsch hydrocarbon synthesis stage tail gas to the Fischer-Tropsch hydrocarbon synthesis stage, to obtain high overall $CO + CO_2$ conversions in the Fischer-Tropsch hydrocarbon

synthesis stage. For the Fischer-Tropsch hydrocarbon synthesis stage, overall CO + CO₂ conversion may be at least 80 %, preferably at least 85 %.

The ratio of the Fischer-Tropsch hydrocarbon synthesis stage tail gas recycle to the tail gas from the DME synthesis stage fed to the Fischer-Tropsch hydrocarbon synthesis stage may be between about 1 : 0.5 and about 1 : 1.5, e.g. about 1 : 1.

The Fischer-Tropsch hydrocarbon synthesis stage may operate at a temperature of at least 320 °C. Typically, the Fischer-Tropsch hydrocarbon synthesis stage operates at a temperature between about 320 °C and 350 °C, e.g. about 350 °C, and at an operating pressure in the range 10 bar to about 50 bar, i.e. at about the same operating pressure as the DME synthesis stage, but preferably lower.

The Fischer-Tropsch hydrocarbon synthesis stage is thus a low chain growth synthesis stage, which typically employs a two-phase fluidised bed reactor and which does not produce a continuous liquid hydrocarbon product phase in the fluidised bed reactor.

The Fischer-Tropsch catalyst used in the Fischer-Tropsch hydrocarbon synthesis stage may be an iron catalyst, and is preferably a promoted iron catalyst. The catalyst may be promoted for activity and/or selectivity.

The DME synthesis stage tail gas fed to the Fischer-Tropsch hydrocarbon synthesis stage may comprise hydrogen, carbon monoxide and carbon dioxide with a syngas number (SN) between about 1.85 and about 2.15, typically between about 1.9 and about 2.1, e.g. about 2.

The process preferably includes a separation stage to separate light hydrocarbons, e.g. C₂-C₄ hydrocarbons, from the Fischer-Tropsch hydrocarbon synthesis stage tail gas. These light hydrocarbons may be converted, together with the DME product, into light olefins in the light olefins production stage.

The process may include treating the condensed liquid hydrocarbons from the Fischer-Tropsch hydrocarbon synthesis stage, to provide a light hydrocarbon

fraction, including naphtha, which may be converted, together with the DME product, in the light olefin production stage to light olefins, and to provide a diesel fraction.

The process may include a diesel hydrotreatment stage to produce high quality diesel motor fuel from one or more diesel fractions produced by the process of the invention.

In the light olefin production stage, the DME product and/or the light hydrocarbon fraction from the condensed liquid hydrocarbons produced by the Fischer-Tropsch hydrocarbon synthesis stage and/or the light hydrocarbons from the Fischer-Tropsch hydrocarbon synthesis stage tail gas is converted into light olefins, such as ethylene and propylene. Preferably, a zeolite such as ZSM-5 or a molecular sieve catalyst, preferably a silicoalumina phosphate catalyst is used to produce the light olefins. Suitable silicoalumina phosphate catalysts include SAPO-5, SAPO-8, SAPO-11, SAPO-16, SAPO-17, SAPO-18, SAPO-20, SAPO-31, SAPO-34, SAPO-35, SAPO-36, SAPO-37, SAPO-40, SAPO-41, SAPO-42, SAPO-44, SAPO-47 and SAPO-56, the metal-containing forms thereof, and mixtures thereof.

The invention will now be described, by way of example, with reference to the accompanying diagrammatic drawing which shows a simplified flow sheet of a process in accordance with the invention for synthesising hydrocarbons.

Referring to the drawing, reference numeral 10 generally indicates a process in accordance with the invention for synthesising hydrocarbons, such as Fischer-Tropsch derived diesel and light olefins such as ethylene and propylene.

The process 10 includes a DME synthesis stage 12 comprising an optional methanol reactor 14 and a combined methanol and DME reactor 16. A syngas feed line 18 feeds into a heat exchanger 20 and from the heat exchanger 20 into the optional methanol reactor 14, with a bypass line 22 being provided around the optional methanol reactor 14. A methanol feed line 24 connects the methanol reactor 14 and the methanol and DME reactor 16.

A raw DME product line 26 leaves the methanol and DME reactor 16 and passes through the heat exchanger 20 and a cooler 28 before entering a vapour-liquid separator 30. The vapour-liquid separator 30 is provided with a liquid product line 31 and a tail gas line 36. The liquid product line 31 is fed to a fractionation stage 33 provided with a water withdrawal line 32 and a DME product line 34.

A tail gas recycle line 38 branches from the tail gas line 36 and passes through a compressor 40 before returning to the syngas feed line 18.

The tail gas line 36 passes through an optional heater 42 before entering a high temperature Fischer-Tropsch hydrocarbon synthesis stage 44. A gaseous product line 46 leads from the synthesis stage 44 to a washing column 48 and from the washing column 48 to a three-phase separator 50, via a cooler (not shown). A tail gas recycle line 65 branches from the tail gas line 64 and passes through a compressor 67 before returning to the tail gas line 36 entering the hydrocarbon synthesis stage 44.

The washing column 48 is provided with a heavy oil recycle line 52 and a cooler 54. The heavy oil recycle line 52 is taken from a heavy oil line 56 which leads from a bottom of the washing column 48 to a vacuum distillation stage 58.

A reaction water line 60, a hydrocarbon condensate line 62 and a Fischer-Tropsch hydrocarbon synthesis stage tail gas line 64 lead from the separator 50. A hydrocarbon condensate reflux line 66 is taken from the hydrocarbon condensate line 62 and leads back into the washing column 48.

The tail gas line 64 leads into a refrigeration stage 68 and from there into a separator 70. A tail gas aqueous condensate line 72, a tail gas hydrocarbon condensate line 74 and a wet tail gas line 76 leave the separator 70. The wet tail gas line 76 feeds into a dryer 78. From the dryer 78, a dry tail gas line 80 passes through an optional CO₂ removal stage 81, a heat exchanger 82 and an expansion turbine 84 before entering another separator 86. The dryer 78 is also provided with a water withdrawal line 88.

The hydrocarbon condensate line 62 and the tail gas hydrocarbon condensate line 74 lead to an atmospheric distillation stage 90. From the atmospheric distillation stage 90, a light hydrocarbon fraction line 92 and a diesel fraction line 94 respectively lead to a light olefin production stage 96 and a diesel hydrotreatment stage 98. The diesel hydrotreatment stage 98 is also fed with a diesel fraction line 100 from the vacuum distillation stage 58. A diesel product line 102 leaves the diesel hydrotreatment stage 98 and a heavy oil product line 104 leaves the vacuum distillation stage 58.

A light hydrocarbon line 106 leads from the separator 86 into an olefin purification stage 108 and a fuel gas line 110 leads from the separator 86 and passes through the heat exchanger 82. A light olefins product line 118 leads from the olefin purification stage 108.

The light olefin production stage 96 is fed with the light hydrocarbon fraction line 92 from the atmospheric distillation stage 90, the DME product line 34 from the three-phase separator 30 and a paraffins and heavy hydrocarbons line 112 from the olefin purification stage 108. A water withdrawal line 114 and an olefins line 116 lead from the light olefin production stage 96. The olefins line 116 leads from the light olefin production stage 96 into the dry tail gas line 80, before the heat exchanger 82.

In use, syngas with a syngas number between 1.8 and 2.2, e.g. about 2, is fed along the syngas feed line 18 into the methanol reactor 14 (if present) or the methanol and DME reactor 16, if the methanol reactor 14 is not present. Before entering the reactor 14 or 16, the syngas is heated in the heat exchanger 20 to a temperature of about 200 °C. The syngas, comprising CO, CO₂ and H₂, is typically at a pressure of about 35 bar(g).

The syngas can be derived from natural gas or from solid carbonaceous material. When derived from natural gas, the syngas is typically obtained by subjecting the natural gas to a partial oxidation reforming step or autothermal reforming step operating with a low steam to carbon ratio to produce a synthesis gas with an H₂ : CO ratio of less than 2.4. If necessary, the composition of the syngas is adjusted to obtain

a syngas number between 1.8 and 2.2, e.g. by the addition of an H_2 rich gas obtained from a steam reformer unit.

If the methanol reactor 14 is present, the syngas is contacted with a copper-containing catalyst to produce methanol. The methanol and unreacted syngas are then fed to the methanol and DME reactor 16, by means of the methanol feed line 24, to produce a raw DME product comprising methanol and DME and water. In the methanol and DME reactor 16, the syngas (if the methanol reactor 14 is not present) or the methanol and syngas mixture (if the methanol reactor 14 is present), is contacted with a methanol catalyst and a methanol dehydration catalyst, thereby providing a product mixture with a high DME to methanol ratio. The methanol dehydration catalyst is typically a catalyst comprising alumina or alumina silicates as active compounds.

The raw DME product from the methanol and DME reactor 16 leaves the reactor 16 by means of the raw DME product line 26 and exchanges heat in indirect relationship with the syngas in the syngas feed line 18, by means of the heat exchanger 20, and then passes through the cooler 28, before entering the vapour-liquid separator 30.

In the vapour-liquid separator 30, liquid reaction products are separated from gaseous or uncondensed products and unreacted reactants and removed along the line 31 and any uncondensed components are removed as a tail gas along the tail gas line 36. The liquid reaction products are fed to the fractionation stage 33 where water is separated from a DME product comprising DME and methanol. The water is removed along the water withdrawal line 32. The DME product is removed by means of the DME product line 34. A portion of the tail gas in the tail gas line 36 from the separator 30 is recycled by means of the tail gas recycle line 38 and compressor 40 to the syngas feed line 18. Typically, the ratio of tail gas recycle to syngas is about 1 : 1, providing an overall $CO + CO_2$ conversion in the DME synthesis stage 12 of the order of about 50 %.

The tail gas from the separator 30 not recycled is optionally heated in the heater 42 before entering the high temperature Fischer-Tropsch hydrocarbon synthesis stage 44. The tail gas comprises unreacted hydrogen, unreacted carbon monoxide and carbon dioxide and requires no composition adjustment before entering the

hydrocarbon synthesis stage 44. Preferably, the Fischer-Tropsch hydrocarbon synthesis stage 44 is operated at a lower pressure than the DME synthesis stage 12, so that no additional compression of the tail gas fed to the synthesis stage 44 is required.

The high temperature Fischer-Tropsch hydrocarbon synthesis stage 44 typically comprises one or more two-phase fluidised bed reactors operating at a high Fischer-Tropsch hydrocarbon synthesis reaction temperature typically between about 320 °C and 350 °C. In these fluidised bed reactors, the carbon monoxide, carbon dioxide and hydrogen react to form gaseous hydrocarbons which leave the hydrocarbon synthesis stage 44 along the gaseous product line 46. The catalyst used in the hydrocarbon synthesis stage 44 is a promoted iron catalyst. The operation of a high temperature Fischer-Tropsch synthesis stage, such as the hydrocarbon synthesis stage 44, is well-known to those skilled in the art and will not be described in further detail.

The gaseous hydrocarbons from the hydrocarbon synthesis stage 44 enter the washing column 48 which uses heavy oil, and hydrocarbon concentrate from the separator 50, as a washing liquid. The heavy oil is circulated through the cooler 54 which removes heat introduced by the gaseous hydrocarbons from the hydrocarbon synthesis stage 44.

Gaseous hydrocarbons passing through the washing column 48 leave the washing column 48 by means of the gaseous product line 46 and are cooled in a cooler (not shown) before entering the separator 50. Before entering the separator 50, the gaseous hydrocarbons are thus cooled to a temperature of between about 30 °C and about 80 °C, e.g. about 70 °C. In the cooler and the separator 50, reaction water condenses and, after separation, is removed along the reaction water line 60. Some hydrocarbons also condense to form a hydrocarbon condensate, which is removed along the hydrocarbon condensate line 62. The remaining gaseous hydrocarbons leave the separator 50 as a tail gas, along the tail gas line 64.

In the Fischer-Tropsch hydrocarbon synthesis stage 44, preferably at least 85 % of the CO and CO₂ entering the stage 44 is converted to hydrocarbons. In order to achieve such high conversion rates, a portion of the tail gas in the tail gas line 64 from the separator 50 is recycled, by means of the tail gas recycle line 65 and the

compressor 67. Typically, the ratio of tail gas from the Fischer-Tropsch hydrocarbon stage 44 to tail gas from the DME synthesis stage 12, fed to the Fischer-Tropsch hydrocarbon synthesis stage 44, is about 1 : 1.

The tail gas from the separator 50 which is not recycled to the hydrocarbon synthesis stage 44, is refrigerated in the refrigeration stage 68 typically to a temperature of about 5 °C. The refrigerated tail gas then enters the separator 70, by means of the tail gas line 64. In the separator 70, the refrigerated tail gas is separated into an aqueous tail gas condensate removed along the tail gas aqueous condensate line 72, a tail gas hydrocarbon condensate removed along the tail gas hydrocarbon condensate line 74, and wet tail gas which is removed along the wet tail gas line 76.

The wet tail gas is dried in the dryer 78 and fed by means of the dry tail gas line 80 to the heat exchanger 82 where it is cooled further before passing through the expansion turbine 84 (other expansion or cooling techniques may instead be used), which causes the temperature of the dry tail gas to drop to about -80 °C. If desired, the dry tail gas may first pass through the optional CO₂ removal stage 81 to remove and recover CO₂ from the tail gas, using conventional methods known to those skilled in the art.

The cold dry tail gas from the expansion turbine 84 is fed into the separator 86, where it is separated into light liquid hydrocarbons, predominantly comprising light olefins and paraffins, which are removed along the light hydrocarbon line 106, and a hydrocarbon lean tail gas which is removed along the fuel gas line 110 and which passes through the heat exchanger 82 in indirect heat exchange relationship with the dry tail gas in the dry tail gas line 80. Other more complex heat exchange relationships may also be applied.

The light hydrocarbons in the light hydrocarbon line 106 are further separated by separation methods known to those skilled in the art, in the olefin purification stage 108, to provide a light olefins product which is withdrawn along the light olefins product line 118. Typically, the light olefins product includes ethylene, propylene and butylene. Paraffins, such as C₂-C₄ paraffins and heavier hydrocarbons are removed from the olefin purification stage 108 by means of the paraffins and heavy hydrocarbon line 112.

The hydrocarbon condensate from the three-phase separator 50 and the tail gas hydrocarbon condensate from the separator 70 are fed by means of the lines 62, 74 to the atmospheric distillation stage 90 where the hydrocarbon condensate is distilled into various fractions, as desired. In contrast, the heavy oil from the washing column 48 is fed by means of the heavy oil line 56 to the vacuum distillation stage 58 where it is distilled under a vacuum into various desired fractions.

The vacuum distillation stage 58 produces a heavy oil product which is removed along the heavy oil product line 104 for further processing and/or purification, and a diesel fraction which is removed along the diesel fraction line 100. The atmospheric distillation stage 90 produces a light hydrocarbon fraction, comprising naphtha and other light hydrocarbons, which is removed along the light hydrocarbon fraction line 92, and a diesel fraction which is removed along the diesel fraction line 94. The diesel fractions from the vacuum distillation stage 58 and the atmospheric distillation stage 90 are fed to the diesel hydrotreatment stage 98, which is supplied with hydrogen (not shown), to provide a diesel product which is withdrawn along the diesel product line 102.

The DME product in the DME product line 34, the light hydrocarbon fraction in the light hydrocarbon fraction line 92, and the paraffins and heavy hydrocarbons in the paraffins and heavy hydrocarbons line 112 are fed to the light olefin production stage 96 as a feedstock. The feedstock is passed over a DME dehydration catalyst, such as ZSM-5 or SAPO-34. In the process, the feedstock is dehydrated, producing an aqueous condensate stream which is removed along the water withdrawal line 114, and light olefins which are removed along the olefins line 116. The light olefins typically include ethylene, propylene and possibly butylene and small amounts of aromatics and are fed by means of the olefins line 116, via the heat exchanger 82, expansion turbine 84 and separator 86 to the olefin purification stage 108 for purification before withdrawal along the light olefins product line 118.

Advantageously, a favourable pressure gradient exists between the DME synthesis stage 12 and the high temperature Fischer-Tropsch hydrocarbon synthesis stage 44. Also advantageously, as a result of the presence of the high temperature Fischer-Tropsch hydrocarbon synthesis stage 44, the operating pressure of the DME

synthesis stage 12 can be reduced to a pressure less than 50 bar(g), the methanol reactor 14 can be either totally removed or made smaller and the DME synthesis stage tail gas recycle can be reduced, meaning that the capacity of the compressor 40 can be decreased. In other words, the fact that the DME synthesis stage 12 is followed by the high temperature Fischer-Tropsch hydrocarbon synthesis stage 44 means that the syngas conversion required in the DME synthesis stage 12 can be lower than that required for a conventional standalone DME plant, as the unconverted syngas can be converted to a high degree to valuable hydrocarbons in the Fischer-Tropsch hydrocarbon synthesis stage 44 which is non-equilibrium limited. It is also an advantage of the process 10, as illustrated, that no adjustment of the tail gas from the DME synthesis stage 12 is required before the tail gas can be fed to the high temperature Fischer-Tropsch hydrocarbon synthesis stage 44, and that any CO₂ formed in the DME synthesis stage 12 is reactive in the Fischer-Tropsch hydrocarbon synthesis stage 44. The process 10, as illustrated, furthermore allows co-processing of DME with high temperature Fischer-Tropsch naphtha to produce C₂-C₄ olefins. In the process 10, as illustrated, the yield to light olefins is thus higher than for standalone high temperature Fischer-Tropsch hydrocarbon synthesis plants, and at the same time the capital cost related to DME production is lower than that of a standalone DME plant.

